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(54) Title: IMPROVED, HIGH YIELD BIOHEAP LEACHING OF CHALCOPYRITE COPPER ORES

(57) Abstract: An improved process for the bioheap leaching of copper ores is disclosed. In this process, the bioheap leaching is conducted at below or around $E_h < 550\text{mV}$. Preferably the concentration of Fe^{2+} and Fe^{3+} , which are generated during leaching, are maintained such that the concentration of Fe^{2+} is greater than Fe^{3+} . The process has particular utility in relation to chalcopyrite ores.

Improved, high yield bioheap leaching of chalcopyrite copper ores

Technical Field

This invention relates to the extraction of precious metals, and particularly to the extraction of copper from chalcopyrite ore using biohydrometallurgical processes.

Background Art

Chalcopyrite (CuFeS_2) or copper iron sulfide is a fairly common mineral and one of the chief ores of copper. Its existence in large quantities and in many locations (eg. Chile, Peru, Mexico, Europe, South Africa, USA) makes it a leading source of copper.

To date, extraction of copper from chalcopyrite ores has largely been by pyrometallurgical processes. In these processes, sulphide sulphur is converted to sulphur dioxide which is captured primarily as sulphuric acid. Several hydrometallurgical processes for copper extraction from chalcopyrite have also been developed. These processes in general convert sulphide sulphur to elemental sulphur directly. Notwithstanding the above, a technology has yet to be developed which will allow economic heap leaching of copper from chalcopyrite ores, although there is intense research activity in the field.

It is known that bacterial leaching of some sulphide minerals including chalcocite, covellite and bomite, zinc sulphides and most nickel sulphides occurs rapidly and relatively completely. However, to date, bacterial leaching of chalcopyrites has been only partially effective.

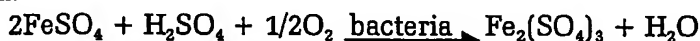
In processes using Acidithiobacillus Ferrooxidans the insoluble copper sulfide mineral is oxidised by the microorganisms to sulfate which is soluble in the aqueous leach media. Any iron present in the copper sulfide substrate is oxidized by the microorganisms to ferric ion (known as an oxidizing agent) and it contributes to the sulfide oxidation step. Oxidation of chalcopyrite can be represented as follows:



The ferric sulfate produced in the above reaction oxidizes metal sulfides (eg. sphalerite)



as the ferric ion is reduced during oxidation of zinc sulphides, it is reoxidized by A.ferrooxidans and in this way the iron redox cycle is closed.



- 5 In the case of A. ferrooxidans, this chemolithotrophic bacteria derives its energy from oxidation of ferrous ion and reduced valence inorganic sulfur compounds and utilizes carbon dioxide for growth when cultured on chalcopyrite.

U.S. Patent Number 06168766 to NIPPON MINING & METALS CO.

- 10 LTD for example discloses a process for leaching copper from copper sulfide using bacteria, which ensures that the rate of leaching of copper increases to reduce the leaching time period and that the rate of leaching of primary copper sulfide contained in ores is increased. The process comprises using an acid leaching solution that includes both or any one of
15 iron oxidizing bacteria and sulfur oxidizing bacteria in a concentration of 10^6 microbes/mL, the acid leaching solution having a redox potential of from 550 to 750 mV and 5g/L or more of iron, the ratio of trivalent iron ions to bivalent iron ions ($\text{Fe}^{3+}/\text{Fe}^{2+}$) in the acid leaching solution being 50 or more.

- 20 According to a patent to GEOBIOTICS, INC. U.S. Patent No. 06110253, a heap preferably having dimensions of at least 2.5 m high and 5 m wide is constructed with chalcopyrite bearing ore. The constructed heap includes exposed sulfide mineral particles at least 25 weight % of which are chalcopyrite. The concentration of the exposed sulfide mineral
25 particles in the heap is such that the heap includes at least 10 Kg of exposed sulfide sulfur per tonne of solids in the heap. Furthermore, at least 50% of the total copper in the heap is in the form of chalcopyrite. A substantial portion of the heap is then heated to a temperature of at least 50°C. The heap is inoculated with a culture including at least one strain of
30 thermophilic microorganisms capable of bioleaching sulfide minerals at a temperature above 50°C. A process leach solution that includes sulfuric acid and ferric iron is applied to the heap. Bioleaching is carried out so that sufficient sulfide mineral particles in the heap are biooxidized to oxidize at least 10 Kg of sulfide sulfur per tonne of solids in the heap and
35 to cause the dissolution of at least 50% of the copper in the heap into the process leach solution in a period of 210 days or less from completion of

the heap. A pregnant process leach solution that contains dissolved copper 1:3 collected from the heap as it drains from the heap. Copper may then be recovered from the pregnant process leach solution.

The difficulty with bacterial leaching appears to be at least twofold.

- 5 The first problem appears to be that in both chemical and biological leaching of chalcopyrite, the rate of dissolution of the ore is uneconomically slow. The other, and perhaps related difficulty appears to be the formation of a physical coating around the copper particle during dissolution, known as a passivating layer, causing the rate of dissolution to plateau. This effect occurs because diffusion of ions to and from the mineral surface is prevented physically by the layer. It is now thought that this precipitate is either iron oxide or Jarosite in nature.

- 10 A silver catalyzed bioleaching process for chalcopyrite has been proposed but it's financial merit is yet to be demonstrated at a commercial scale.

Disclosure of Invention

Accordingly it is an aim of this invention to provide an improved, high yield process for the extraction of copper from chalcopyrite ores.

- 15 A conventional bioheap leaching process may be described as follows.

- Mined copper ores are crushed to an optimum particle size. The crushed ore is mixed with sulfuric acid in an agglomerating device to consolidate the fines with the coarser ore particles and precondition the ore for bacterial development. Water or raffinate (effluent from the solvent extraction-electrowinning circuit) is added to optimize the moisture content for good agglomerate formation. If the ore is not too acid consuming, the acid requirement to precondition the ore can be met by agglomerating with raffinate. Raffinate usually contains a small population of bacteria, which inoculate the ore. The agglomerated and preconditioned copper ore is conveyed to the leach area where it is stacked 6 to 10 m high on a lined pad or on top of previously leached ore. Plastic piping with ventilation holes is placed on the pad or lift to supply air to the bacteria during leaching. Aeration of the bioheap is initiated soon after stacking the agglomerated ore. Low pressure fans supply air to the ventilation system under the ore. The bioheap is irrigated with raffinate at an application rate that does not cause saturation. Pregnant leach solution

(PLS) (effluent containing copper) is collected at the base of the bioheap and is either (1) recycled to the top of a new heap for irrigation (referred to an "intermediate leach solution" or "ILS"), or (2) directed to a SX/EW (solvent extraction/electro-winning) circuit for copper recovery. The raffinate (barren solution from the SX/EW circuit) is returned to the bioheap for irrigation. Leach times vary among the operations, but is typically in the 200-day range for secondary copper ores. Copper recoveries also vary with 75% to 85% recoveries achieved at most operations.

10 In a process such as that described a range of temperatures are possible and therefore the bacteria may be selected from the group of thermophilic or mesophilic and acidophilic bacteria including for example, Acidithiobacillus Ferrooxidans, Thiobacillus Thiooxidans, Leptospirillum Ferrooxidans, Thiobacillum Caldus, Sulphobus Acidocaldarius & Acidianus brierleyi. It is known for example, that these microorganisms will variously having optimum efficiency at different temperatures (A. ferrooxidans at temperatures above 35°C and A. brierleyi at temperatures in excess of 60°C and as high as 80°C).

20 In a "direct leaching" process, the bacteria will be present in the heap or will be inoculated into the heap via the leaching solution or raffinate. In an "indirect leaching" process, the bacteria will be contained in a reaction unit separated from the heap.

Thus, in one aspect of the invention, in a process for bioheap leaching such as that described hereinabove which is directed at the extraction of copper from chalcopyrite, the invention provides the improvement of maintaining the reduction potential at below or around Eh < 550mV. To do this, attention must be paid to the relative concentration of Fe^{2+} / Fe^{3+} with a particular emphasis on maintaining high levels of Fe^{2+} in the process. This may be achieved for example, in the situation that the heap contains the organisms, ie. in a direct leaching process, by maintaining very limited levels of oxygen in the heap. It is anticipated that in this case the temperature of the heap would need to be maintained at around or above 55°C.

35 In the case of an indirect bioleaching process bacterial oxidation may occur separately from the heap site and oxygen supply to the heap would need to be prevented so as to prevent oxidation of ferrous iron to

ferric iron. In this case it is anticipated that the temperature of the heap would need to again be maintained at temperatures around or above 55°C.

In another aspect of the invention, in a process for bioheap leaching such as that described hereinabove which is directed at the extraction of copper from chalcopyrite, there is provided the improvement of conducting a combined direct and indirect leaching process on a heap including both chalcopyrite and another copper sulphide ore such as chalcocite. In this situation, it is anticipated that a bacterial oxidation process could be conducted externally of the heap in a separated process unit such that in the extraction of copper from chalcocite, ferric iron is consumed increasing the relative levels of ferrous iron, and then in the extraction of copper from chalcopyrite, ferrous iron is consumed requiring the bacteria to effect oxidation to ferric iron so as to enable a continuous process. In this process, it is envisaged that the temperature of the heap would need to be maintained around or above 60°C.

The invention is predicated on the discovery that the chalcopyrite dissolution rate is strongly dependent on the reduction potential (Eh) in solution. The invention is further predicated on the discovery that high concentrations of ferric ions suppress the leaching of copper from chalcopyrite and that conversely, high levels of ferrous ions have an enhancing effect on the chalcopyrite extraction process. It is also postulated that copper extraction from chalcopyrite ores is most efficient at high temperatures, for example, in excess of 50°C.

One further difficulty in current models of bioheap leaching for application to the extraction of copper from chalcopyrite ores lies in the fact that conventional methods for extracting the copper from solution such as solvent extraction do not handle the high temperatures required to sustain the thermophilic / mesophilic bacteria. In order to adapt the leachate solution to processing by conventional solvent extraction stages, the temperature of the leachate must be reduced. However, in so doing, the biomass is substantially reduced requiring downstream adjustment to restore bacterial levels sufficient to effect the restoration of ferrous iron levels in the heap.

Thus, it is a further aim of this invention to provide alternate means of solvent extraction in a bioheap leaching process whereby the biomass is not substantially negatively effected.

There is thus provided in a bioheap leaching process as hereinbefore described directed at the extraction of copper metal from copper ores the improvement whereby the solvent extraction process is effected by an ion exchange - electrowinning stage.

- 5 This solution has the dual advantage that the ion-exchange - electrowinning process is susceptible of effective utilisation at higher temperatures, and that further, since it is a solid-based process, not liquid based, it is more environmentally friendly than traditional means.

- 10 It will be appreciated that this invention is not limited to the specific embodiments herein and may be potentially applied to other heap leaching processes as well as to other ores.

CLAIMS:

1. In a process for the bioheap leaching of copper ores in which:
 - (a) the ore is crushed to an optimum particle size;
 - 5 (b) the crushed ore is mixed with sulfuric acid in an agglomerating device to consolidate fines with coarser ore particles and precondition the ore for bacterial development;
 - (c) water or a raffinate, is added to the agglomerating device to optimize the moisture content for good agglomerate formation;
 - 10 (d) the agglomerated and preconditioned ore is conveyed to a leach area where it is stacked on a lined pad or on top of previously leached ore to form a bioheap, the pad or leached ore being provided with plastic piping with ventilation holes to supply air to the bacteria during leaching;
 - (e) aeration of the bioheap is initiated soon after stacking the agglomerated
15 ore;
 - (f) the bioheap is irrigated with raffinate containing bacteria;
 - (g) pregnant leach solution is collected at the base of the bioheap and is either recycled to the top of a new bioheap for irrigation or directed to a circuit for copper recovery; and
 - 20 (h) the raffinate from the copper recovery circuit is returned to the bioheap for irrigation; the improvement comprising:
 - (i) maintaining the reduction potential under which the bioheap leaching is conducted at below or around $E_h < 550\text{mV}$.
2. The process of claim 1 wherein the ore is chalcopyrite.
- 25 3. The process of claim 2 wherein the concentration of Fe^{2+} and Fe^{3+} , which are generated during leaching, are maintained such that the concentration of Fe^{2+} is greater than Fe^{3+} .
4. The process of claim 3 in which the bioheap leaching is a direct leaching process and the concentration of Fe^{2+} and Fe^{3+} is maintained by
30 limiting levels of oxygen in the bioheap.
5. The process of claim 3 in which the bioheap leaching is an indirect leaching process and the concentration of Fe^{2+} and Fe^{3+} is maintained by limiting levels of oxygen supply to the bioheap.
6. The process of claim 4 or claim 5 wherein the bioheap is maintained at
35 a temperature in excess of 50°C .

7. The process of claim 6 wherein the bioheap is maintained at a temperature at or around 55°C.
8. The process according to any one of claims 1 to 7 wherein the circuit for copper recovery comprises an ion exchange - electrowinning stage.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU02/00250

A. CLASSIFICATION OF SUBJECT MATTERInt. Cl. ⁷: C22B 3/18, 15/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC⁷ AS ABOVE AND IPC⁴ C22B 3/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DWPI: IPC as above and key words leach, copper, chalcopyrite, CuFeS₂, Potential, Eh; USPTO: C22b 3/18 and key words chalcopyrite, CuFeS₂, heap**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4571387 (Bruynesteyn et al.), 18 February 1986 Column 2, lines 16- 28; column 4, line 21- column 5, line 54; Claims 2, 3, 11	1- 8
P, Y	WO 01/31072 A1 (Pinches et al.), 3 May 2001 Page 1, line 17- page 2 line 7; page 5, line 24- page 6, line 5; page 14, lines 9- 16; page 16, lines 7- 24; page 17, line 16- page 18, line 2; claim 11	1- 8
Y	Derwent abstract Accession No. 98-018951/02, Class D16, M25, ZA 9701307 A (Mintek) 29 October 1997 Abstract	1- 8



Further documents are listed in the continuation of Box C



See patent family annex

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INTERNATIONAL SEARCH REPORT

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Derwent Abstract Accession No. 98-590026/50, Class D16, M25 JP 10265864 A (Nikko Kinzoku KK), 6 October 1998 Abstract	1- 8
Y	"Redox Potential- Controlled Bacterial Leaching of Chalcopyrite Ores" by Ahonen et al., pp 571- 578, "Bio-hydrometallurgical Technologies", Minerals, Metals & Materials Society 1993. ISBN 0873392523 (set). pp 573, 577	1- 8
Y	US 6146444 (Kohr), 14 November 2000 Column 2, lines 15- 41; column 3, lines 18- 25; column 4, lines 14- 38; column 6, lines 49- 56	1- 8
Y	US 6107065 (Kohr), 22 August 2000 Column 2, line 48- column 3, line 3; column 3, lines 23- 29; column 4, lines 30- 40	1- 8
Y	US 6086656 (Kohr), 11 July 2000 Column 2, line 49- column 3, line 4; column 3, lines 25- 31; column 4, lines 22- 42; column 18, table 3; column 19, table 4; columns 21& 22, table 6; column 24, table 8	1- 8
Y	US 5873927 (Schaffner et al.), 23 February 1999 Column 2, lines 4- 20; column 5, lines 5- 20; column 6, lines 48- 67; column 11, lines 7- 20; Fig 1	1- 8
Y	US 5779762 (Kohr et al.), 14 July 1998 Column 2, line 24- column 3, line 3; column 7, lines 4- 13; columns 17 & 18, table 3; column 18, table 4; column 19, table 5; column 20, table 6	1- 8
Y	US 5676733 (Kohr) 14 October 1997 Column 3, line 40- column 4, line 2; column 4, lines 14- 37; column 6, lines 47- 56	1- 8